STANFORD UNIVERSITY LIBRARY
AUG 9 1928

THE ELECTROLYTIC PREPARATION

OF

HIGHLY CONCENTRATED ALKALI AMALGAMS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY.

BY

CLARE S. MARTIN, B.S., M.S.

The Ohio State University
1923.

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

3781
O37M

UNCLASSED

THE ELECTROLYTIC PREPARATION

OF

HIGHLY CONCENTRATED ALKALI AMALGAMS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY.

BY

CLARE S. MARTIN, B.S., M.S.

The Ohio State University

1923.

ACKNOWLEDGMENT

The writer wishes to express to Doctor James R. Withrow, Chairman of the Committee, his appreciation and gratitude for the selection of this topic, and for his valuable suggestions and encouragements during the progress of this work.

CONTENTS

I. Introduction 8
II. Review of the literature 10
III. Factors influencing concentration of potassium amalgams 12
(a) Clogging of the porous cup 13
(b) Depletion of the electrolyte 18
(c) Effect of temperature 20
(d) Electrolysis at high temperatures 25
1. Experiments with the Shepherd method 25
2. Experiments with the Smith-Bennett method 25
(e) Equilibrium as a factor 28
IV. Notes on other amalgams 29
(a) Sodium amalgam 29
(b) Barium amalgam 30
(c) Calcium amalgam 30
1. Electrolysis at high temperatures 30
2. Electrolysis in non-aqueous solutions 31
V. Conclusions 35

THE SIGNIFICANCE AND IMPORTANCE OF THE ELECTROLYTIC PREPARATION OF ALKALI AMALGAMS

The alkali amalgams are of considerable importance as a reducing agent in Organic chemistry and find extensive use in the manufacture of the caustic alkalis, and in Physical-Chemical studies.

In the industries, where it is sometimes necessary to prepare tons of alkali amalgam for reduction purposes in certain organic reactions, the amalgam is made by adding the alkali metal directly to mercury. But potassium and sodium combine with mercury with great evolution of heat, and sometimes result in severe explosions. An alternative method of preparation is therefore much to be desired.

The electrolytic method of preparing amalgams is free from the danger of explosion, and if sufficiently concentrated amalgams could be made by this method, it would be of great value as a means of avoiding injury to the workmen in the plant.

The electrolytic method of preparing amalgams also offers the best method of obtaining the alkali metals in a high degree of purity for precision measurements. For instance, Theodore William Richards prepared his potassium compounds for the investigation of the atomic weight of potassium by first making the potassium amalgam electrolytically. Methods which will produce a more concentrated amalgam by electrolytic deposition of the metal in mercury are therefore of value to the research chemist.

STATEMENT OF THE PROBLEM

The problem assigned for this investigation was:—The Factors Limiting The Concentration Of Potassium In Electrolytically Prepared Potassium Amalgams, and The Preparation If Possible Of More Highly Concentrated Potassium Amalgams Than Are Recorded In The Literature, Or Have Been Prepared In Previous Studies In This Laboratory.

RESULTS OF THIS INVESTIGATION

The result of this investigation has been to reach a definite decision in the maze of claims regarding the relative value of the various limiting factors in the electrolytic preparation of amalgams.

The exhaustion of the electrolyte, changes in the nature of the electrolyte, the clogging of the pores of the cup in the Shepherd method, equilibrium between the rate of formation and the rate of decomposition of the amalgam at ordinary temperatures, have been eliminated as essential limiting factors.

By proper manipulation and control of temperature, sodium, potassium, and calcium amalgams have been made electrolytically with a higher concentration of metal in the mercury than any previously recorded in the literature.

A careful study of the literature followed by experimental evidence proves conclusively that the phase rule operates to fix a definite limit to the concentration of metal in mercury at any given temperature. Temperature is therefore the primary limiting factor.

I. INTRODUCTION

Amalgams are usually prepared either by direct union, or by elecrolysis. In the first method the metal is added a little at a time to the mercury which is heated a few degrees above room temperature. In the second method, a solution of a salt of the metal or a solution of the hydroxide is used as an electrolyte, and mercury is made the cathode. The metal ions are driven into the mercury by the current, and combine with the mercury to form the amalgam.

Amalgams which are to be used for organic reductions are usually prepared by direct union because this method is more economical of time and materials. However, most metals combine with mercury with explosive violence, and precautions must be taken to prevent accidents. There is no danger of explosion with the electrolytic method.

In the Whiting and Castner cells which are employed in the electrolytic manufacture of caustic soda, an amalgam is first produced by the electrolysis of the brine, and the sodium extracted from the mercury by water. In this process economy of current requires that the concentration of sodium be kept very low because the resistance of the cell rises rapidly with the increase of the sodium in the mercury.

Aside from any industrial value which it may have, the problem of increasing the concentration of metal in alkali amalgams has aroused considerable interest in the literature where the electrolytic method has been studied. It has been found easy to introduce any desired amount of alkali metal into mercury by the method of direct union. There would appear therefore to be no reason why the same could not be done by electrolytic methods. But where electrolytic mthods have been tried, it has not been possible to obtain more than two or three per cent by weight of the alkali metal in the mercury. A number of limiting factors have been suggested in the literature to account for the low yields so obtained.

The object of this investigation was to examine in a purely

qualitative way the various limiting factors which have been suggested, in order to determine what ones are vital obstructions in the method, and if possible to obtain more highly concentrated alkali amalgams by electrolytic methods than have heretofore been possible.

Potassium amalgam was chosen for investigation not only because it is relative easier to work with, but because amalgams of this metal have been more fully studied in the literature. It seemed probable that whatever factors were found to control the concentration of potassium amalgam would apply in a like manner to the other alkali amalgams.

Three modifications of electrolytic preparation have been in use. In the Kerp method (Zeit. Anorg. Chem. 25, 1-71, 1900) the cathode is a fine stream of mercury flowing from a dropping funnel through the electrolyte. In the modification which has come to be known as the Smith-Sennett method (Jour. Amer. Chem. Soc. 32, pp. 622, 1900) the cathode mercury rests on the bottom of a suitable glass vessel with the electrolyte in contact above the mercury. Shepherd's method (Jour. Phys. Chem. 7, 29, 1903) separates the mercury and the electrolyte by means of a porous diaphram, such as an ordinary clay cup.

The Kerp method, though greatly simplified by Giesy and Withrow (Jour. Ind. Eng. Chem. 15, 57, 1923) has the objection that the small orifice from which the mercury flows easily becomes plugged with crystals of amalgam. Aside from this factor, there is no reason for believing that the limiting conditions would differ from those of the Smith-Bennett method. Since the latter method offers easier manipulation, the Kerp method was not used. The porous cup of the Shepherd method, however, introduces a number of complications which it was necessary to investigate.

II. REVIEW OF THE LITERATURE

Amalgams are generally regarded in the literature (Abegg, Handbuch der Anorganische Chem, II Band, 2 Abteilung, pp. 569) (Mellor, Modern Inorganic Chemistry, pp. 342) as compounds of mercury and a metal, in which mercury behaves somewhat like water of hydration in salts. Mellor gives a curve probably derived from Kurnakow (Zeit. Anorg. Chem. 23, 439, 1900) of the concentration of potassium in mercury, plotted against the freezing temperature of the solution. Breaks along the curve are regarded as corresponding to definite chemical compounds.

These are: KHg_9, M.P. 70°c. K_2Hg_9, M.P. 173°c. K_3Hg_8, M.P. 204°c. KHg_2, M.P. 278°c. KHg, M.P. 178°c.

In previous work, other compounds of potassium have been claimed, such as KHg_{12} (Kraut and Popp, Lieb. Ann., 159, 188, 1871), Smith & Bennett, Jour. Amer. Chem. Soc. 32, pp. 622) and KHg_4 (Bertholot, Ann. Chim. Phys. (5) 18, pp. 442, 1879). These amalgams range from 1.6% to 16.2% by weight of potassium, and were prepared by direct union of the potassium and mercury.

No such high concentration of potassium is recorded in the literature for potassium amalgams made electrolytically. Shepherd, using his porous cup method (Jour. Phys. Chem. 29, 1903) obtained the highest concentration of electrolytically prepared potassium amalgam recorded up to that time. He made an amalgam which analyzed 1.6% by weight of potassium. This corresponds approximately to the formula KHg_{12}. Shepherd states that at this concentration, the amalgam hardened in the cup, and that for this reason a more concentrated amalgam could not be obtained. A few years previous to this time, Kerp (Zeit. Anorg. Chem. 17, pp. 284, 1898) had attained nearly the same concentration by his method of preparation. Kerp and Bottger (Zeit. Anorg. Chem. 25, pp. 1, 1900) in their investigation of potassium amalgams, prepared at least one amalgam of the formula KHg_{12} using Kerp's method, and in the same paper stated that a more concentrated amalgam was not to

be prepared by electrolytic methods because of the manipulative difficulties involved. They, like others, made their more concentrated amalgams by melting together mercury and metallic potassium. Smith and Bennett (Jour. Amer. Chem. Soc. 32, pp. 622, 1910) record obtaining a potassium amalgam analyzing as high as 1.7% potassium. The highest concentration recorded anywhere in the literature was obtained by Bain and Withrow (Jour. Phys. Chem. 25, pp. 535, 1921). Using the Smith-Bennett method they were able to obtain a concentration of 2.35% K.

Bain and Withrow do not state that the 2.35% amalgam was solid during electrolysis, thus limiting the concentration of the amalgam. Instead, they suggest the exhaustion of the electrolyte as the probable chief limiting factor.

In view of these ideas, on the one hand of the impossibility of electrolytically preparing concentrated amalgams because of the difficulties involved, and on the other hand, in view of the conflicting ideas on the reasons for low concentrations, and in view of the small amount of potassium attained in even the strongest amalgams, it was decided to thoroughly investigate the obstructing factors, remove them if possible, and prepare more concentrated amalgams.

As a result of several previous investigations in this laboratory on related problems, it was realized that Kerp and Bottger were probably correct in emphasizing the seriousness of the manipulative difficulties involved. This was an added incentive in attacking the problem.

III. EXPERIMENTAL INVESTIGATION OF THE FACTORS INFLUENCING CONCENTRATION

In the literature three factors have been suggested to account for the low yield attainable by electrolytic methods.. These may be listed as:—1st., Depletion of metal ions in the electrolyte. 2nd., The setting up of a condition of equilibrium between the rate of formation of the amalgam by the current, and its decomposition by the water of the electrolyte. 3rd., Formation of a solid amalgam.

Complications introduced by the porous cup in the Shepherd method. In addition to these, the use of the porous cup adds as limiting factors the plugging of the pores of the cup, and the disintegration of the cup itself during electrolysis.

Because of the action of the electrolyte on the amalgam produced by the reaction, the separation of the electrolyte and the amalgam by a porous membrane as in the Shepherd method should offer a more efficient method of preparation since it may reduce the equilibrium factor to zero. The difficulty lies in finding a suitable membrane. Water cannot be completely excluded from the amalgam because some water molecules are carried through the cell walls to the mercury, along with the metal ions. The more porous the cell walls, the greater is the amount of water carried through under certain conditions. On the other hand, if the walls are made less porous to cut down this so-called water of electrosmosis, the resistance of the cell to the passage of the electric current is also increased, and a higher voltage must be used to drive the metal ions through the cell walls and into the mercury. The first effect of increased resistance of the cell, as was found in this investigation, was to raise the temperature. The water of the electrolyte boiled off rapidly, and had to be constantly replaced. It was also found that with some electrolytes, notably KOH solutions, this may lead to excessive foaming. The heat liberated was even found to be sufficient to volatilize a considerable portion of the mercury in the cell, and this made it necessary to take precautions to prevent this loss, and to avoid mercury poisoning.

The fact that no one in the literature has called attention to difficulties with excessive foaming, or to loss of mercury through volatilization makes it probable that previous investigators have not attempted to electrolyze solutions at the high temperatures employed in the investigation. As a matter of fact, it was thought necessary to use cooling baths in order to keep the temperature

down, the idea being that at higher temperatures the rate of decomposition of the amalgam by the electrolyte would be speeded up to such an extent as to interfere with the production of the amalgam. Smith and Bennett, (Jour. Amer. Chem. Soc. 31, pp. 799, 1909), Theodore William Richards, (Jour. Amer. Chem. Soc. 29, pp. 623, 1907), Giesy and Withrow, (Jour. Ind. End. Chem. 15, pp. 57, 1923), thought it advisable to cool the electrolyte. Bain and Withrow (Jour. Phys. Chem. 25, 535, 1921) thought that the unsolved problem of electrolytically making calcium might be met by electrolyzing at low temperatures.

A. **Plugging of the pores of the cup as a limiting factor in the Shepherd method.** If a cell is chosen with sufficiently fine pores to cut down the water of electrosmosis to any extent, the pores rapidly become plugged, and the flow of current ceases. This plugging of the pores comes from two sources. 1st., From the inside, due to the formation of crystals of the amalgam, which have a tendency to cling to the walls of the cup. 2nd., From the outside, due to products of decomposition in the electrolyte. These vary with the conditions of the experiment. In this work plugging of the pores was observed to be due to deposits on the cell of KOH or NaOH; to relatively insoluble chlorates or perhaps hypochlorites, and to colloidal silica from the disintegration of the porous cup.

Three types of porous cups were used in experiments with the Shepherd method. Of these, white clay cups 7 cm. in depth by 2 cm. in diameter were found unsatisfactory for long runs. Cups of red terra cotta measuring 7 cm. by 4 cm. were also unsatisfactory. Not only did the walls plug up easily, but under the conditions of the experiments they disintegrated too rapidly to permit runs to be made which lasted over two hours. Alundum cups measuring 2½ cm. inside diameter by 7 cm. in depth were found to be fairly satisfactory. They permitted longer runs to be made and showed little tendency to clog. It was found possible to make more concentrated amalgams in less time with these cups, but the water of electrosmosis gave more trouble.

The set-up of the apparatus used is shown in figure I, and in the accompanying photograph. Figure II is a wiring diagram of the apparatus. Approximately 175 grams of mercury was placed in the cup. The cup with its contents was placed in a 250cc. pyrex beaker, and elevated above the bottom of the beaker by resting on an inverted porcelain crucible. By this means, the surface of the mercury was kept above the level of the electrolyte as recommended

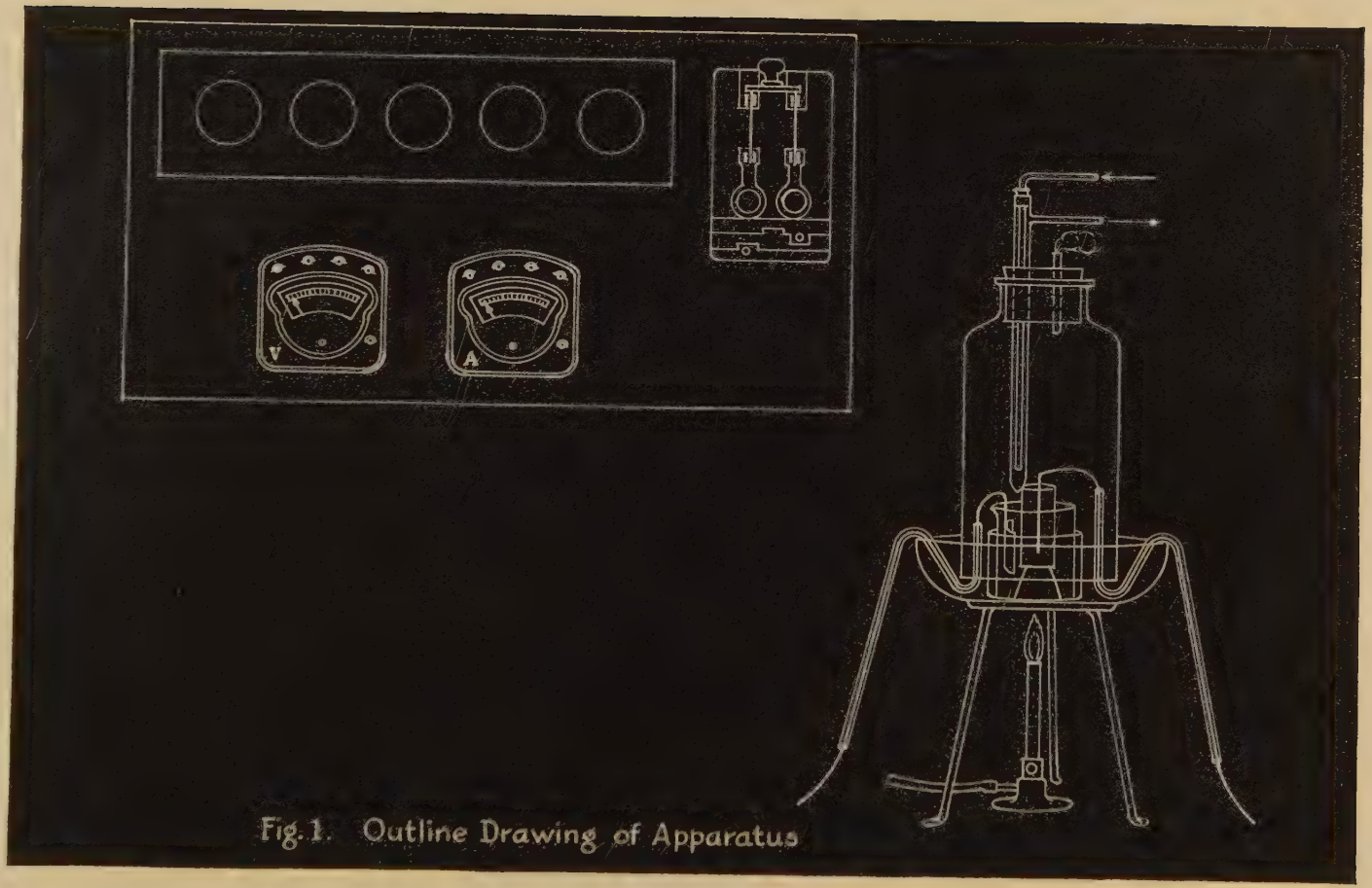


Fig. 1. Outline Drawing of Apparatus

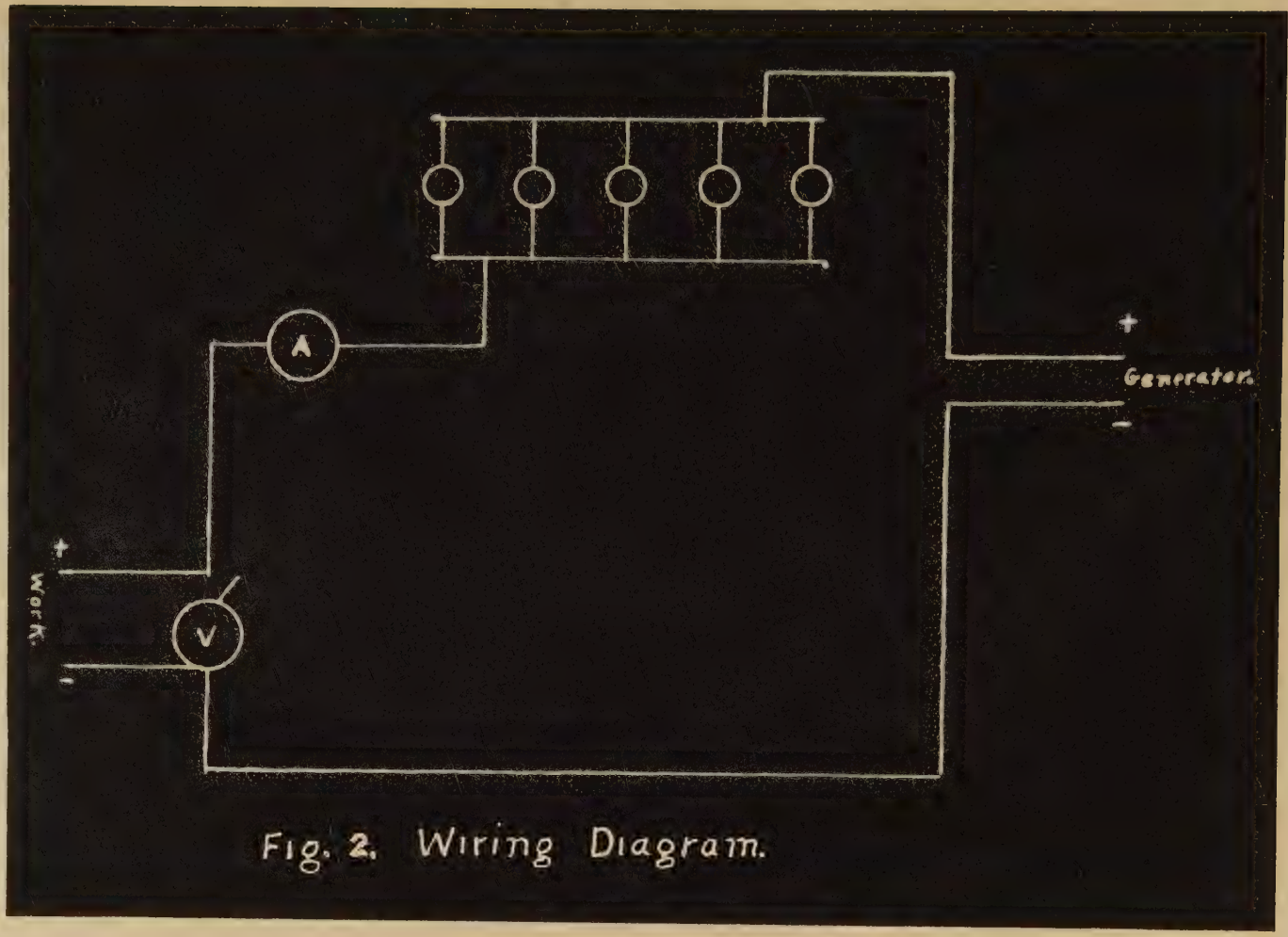


Fig. 2. Wiring Diagram.

by Shepherd. (Jour. Phys. Chem. 7, pp. 20, 1903). This arrangement is intended to allow the crystals of amalgam as they form to rise to the surface of the mercury where they will not plug the pores of the cup. Saturated solutions of KCl, K_2SO_4, and 10% solutions of KOH were used as electrolytes. From 100cc. to 200cc. of solution was placed in the beaker surrounding the cup, and covering the bottom of the cup to a depth of about 1½ cm. A platinum flag electrode 4x8 cm. was used as the anode, and the cathode connection made by dipping a platinum wire into the mercury.

Chlorine fumes liberated in the electrolysis of KCl were disposed of by the following arrangement: An iron dish, ten inches in diameter was filled with sand. By placing an iron collar in the center of the dish, a cavity could be made in the sand in which to place the beaker and its contents. The beaker was covered with a bell jar with the bottom edge buried in the sand. Later on it was found better to use a five pint reagent bottle with the bottom cut off. The mouth of the cover was provided with a two-holed rubber stopper through which passed an outlet tube for drawing off the chlorine, and an inside condenser whose purpose was to condense the water vapor and return it to the beaker. Connection with the source of current was made by passing wires through curved glass tubes which curved under the rim of the bell jar or cover.

The current was controlled by means of a lamp bank placed in the line, and by a rheostat at the generator. Current values were indicated by a standard Weston laboratory voltmeter and ammeter. In general, 3-5 amperes of current at 8-12 volts was used. However, owing to the very rapid fluctuation of current, the current value was only approximately determined. The resistance of the cell changed rapidly, due to the change in the condition of the amalgam and the electrolyte, and to the gradual closing of the pores of the cup.

In a series of forty-two runs made with the cups, it became evident that while the cells usually clogged after a run of about two hours, still, this was not an important factor in controlling the concentration. Two facts were observed which led to this conclusion. In the first place clogging did not always occur, and in these cases, it was still found impossible to obtain more than an ordinary concentration of alkali metal in the mercury. Table No. I shows the effect of the duration of the run on the concentration attained.

TABLE No. I

Effect of Time on Concentration

Run No.	Cell No.	Amps.	Volts	Minutes Time	Freezing Temp.	Per Cent Potassium
6	14	3	12	105	65°c.	2.2
6	14	3	12	150	65°c.	2.2
6	14	3	12	180	65°c.	2.2
6	14	3	12	300	65°c.	2.2
21	32	2	12-20	120	100°c.	2.65
21	33	4-6	10-14	300	80°c.	2.45
21	36	4-5	10-12	360	80°c.	2.45
38	A1	4-8	8-12	40	65°c.	2.2
38	A1	4-8	8-12	120	65°c.	2.2
38	A1	4-8	8-12	450	65°c.	2.2
39	A2	4-5	10-20	195	65°c.	2.2
39	A2	4-5	10-20	285	80°c.	2.45
39	A2	4-5	7	400	80°c.	2.45
39	A2	4-5	7	460	80°c.	2.45

The table shows that after a certain maximum concentration was reached, continued electrolysis did not add to the amount of alkali metal in the mercury. In other words, if the pores of the cup had been clogged after two hours run, this would have stopped the inflow of metal ions, but it would not have been an essential limiting factor in the concentration because the maximum concentration would have been reached before clogging occurred.

It should be stated that the per cent of potassium given in the last column was calculated from Kurnakow's temperature-concentration diagram, (Zeit, Anorg. Chem. 23, pp. 439, 1900), using the observed melting point. Whenever it was desired to know accurately the composition of an amalgam, it was analyzed by the method employed by Smith and Withrow. (Jour. Amer. Chem. Soc. 29, pp. 321, 1907). The values so determined were found in close agreement with the values indicated on the Kurnakow temperature-concentration diagram.

That the clogging of the pores of the cup was not an essential limiting factor was further demonstrated by removing the amalgam from a ruined cup, and continuing the run with a fresh tested cup. This procedure is illustrated by run 21 in Table I. Additional potassium content was not obtained, showing that the maximum amount, under the conditions of the experiment had been reached

before the plugging of the pores occurred. The observation was repeated a number of times.

It is of interest to note in this connection, that when once the pores of the cell had become plugged, the cell could not be restored by further treatment. Boiling in strong acids and in KCl solutions; long soaking in distilled water; reversing the direction of the current; and even grinding away a considerable portion of the cell wall were among the expedients tried. It is probable that the clogging is due not only to the deposit of colloidal particles (such as silica) in the fine openings, but also to changes in the structure of the cell wall itself which are brought about by the electroylsis. Microscopic examination indicates this to be true.

B. **Depletion of the electrolyte as a limiting factor in the concentration of amalgams.**

Bain and Withrow have raised the question as to whether exhaustion of the electrolyte may not have limited the concentration in the amalgams made by them. (Jour. Phys. Chem. 25, pp. 535, 1921). They state that at the end of a long run, using KCl, they could not detect the odor of chlorine which should have been evolved if the electrolyte were not exhausted.

It can readily be seen that convenience would govern the amount of electrolyte used, and therefore in a series of experiments, the investigator would tend to use about the same quantity of materials. This would be true not only for a series of experiments by the same man, but others would tend to fall into the same procedure. We find that in the literature, the amounts of electrolyte and mercury used, and the current employed does not vary greatly with different experimentors, and the conclusion of Bain and Withrow seemed a reasonable one.

However in a series of twenty-eight runs with KCl solutions under conditions similar to theirs, and from which fourteen samples of potassium amalgam were made, no point was reached where there was a cessation of the evolution of chlorine. This point was tested several times during each run. The odor of free chlorine coming from the cell was always noticeable when the bell jar was lifted, and the air above the cell was fanned away. As a further qualitative test, white fumes were produced with a strip of filter paper moistened with NH_4OH. Likewise, a strip of filter paper moistened with 10% KI solution turned brown due to the setting free of iodine. This test was so pronounced as not to require the use of starch iodide.

It should be mentioned at this point however, that we observed the building up of a toleration for the odor of chlorine where it was allowed to escape into the laboratory in not too great quantities, so that the odor was scarcely evident. It is suggested that this might explain the failure of Bain and Withrow to observe the evolution of chlorine towards the end of an experiment.

The following simple calculation also shows that the exhaustion of the electrolyte was not a probable limiting factor. It is reasonable to assume from Kurnakow's temperature-concentration diagram (see Figures III and IV) that the potassium amalgams usually obtained by electrolysis, and hardening at 60-70 degrees represent a compound of the formula KHg_8. This compound would have a potassium content of approximately 2.38% which is slightly above the maximum concentration obtained by Bain and Withrow. If these authors used only 100cc. of saturated KC1 solution, there would have been present in the solution at least 18 grams of potassium. The 250 grams of amalgam made by them would require only about six grams of potassium for a 2.3% concentration. These authors must have been deceived on chlorine evolution, or some other unknown factor entered into their work.

The depletion of the electrolyte as an important factor was eliminated in still another way:—Using the Shepherd porous cup method, with a current of 5-8 amperes at 8-12 volts, we were able to produce in an hour and a half, potassium amalgams hardening at 65°-70°c. Continuing the run two or three hours longer failed to increase the hardness of the amalgams, as has been shown in Table I. In order to test the electrolyte, the porous cup was removed, and a fresh cup charged with 165 to 170 grams of mercury substituted. The result was an additional yield of amalgam, thus showing that the electrolyte had not been depleted. Two of the three tests made gave a second yield of 165-170 grams of potassium amalgam hardening from 65°-70°c.

KC1 was used as an electrolyte in order that the results might be comparable with those of previous workers. However, it is not the best electrolyte to use. The reactions are extremely complicated, the primary products of the electrolysis of KC1 being K, C1, H, KOH, and the secondary products being some if not all of the oxygen acids of chlorine. The influence of these on the progress of the electrolysis, together with the effect of temperature and current conditions on the amount and character of the products formed during the electrolysis would have made an interesting study in itself. But when it was shown that the conditions in the electrolyte

were not important factors in limiting the concentration of potassium in the mercury, no further time was spent on an investigation of the effect of these by-products on cell efficiency.

C. **Temperature as a Limiting Factor in Controlling the Concentration of Potassium in the Amalgam.**

In the earlier literature as shown in the following citations, electrolytically prepared amalgams appear not to have exceeded a concentration of about 1.6% potassium. This corresponds to the formula KHg_{12}, and was obtained by several investigators at temperatures ranging from 25°-95°c. For example, Kerp (Zeit. Anorg. Chem. 17, pp. 284, 1898) attained this value. Kerp and Bottger (Zeit. Anorg. Chem. 25, pp. 1, 1900) in their investigation of potassium amalgams prepared a sample of this strength by electrolysis, and at that time stated that by electrolytic methods a more concentrated amalgam was not to be obtained. They, like others, made their more concentrated amalgams by melting together mercury and metallic potassium. Smith and Bennett (Jour. Amer. Chem. Soc. 32, pp. 622, 1910) record obtaining a potassium amalgam with as high as 1.7% potassium. Smith and Withrow (Jour. Amer. Chem. Soc. 29, 324, 1907) reached a value of 1.66% by electrolyzing KNO_3 solutions, and Bain and Withrow (Jour. Phys. Chem. 25, pp. 535, 1921) attained the high concentration of 2.31% by electrolyzing KC1 solutions at 108 degrees centigrade.

In a series of investigations on the compounds of potassium and mercury by Kerp (Zeit. Anorg. Chem. 17, pp. 284, 1898), by Kerp and Bottger (Zeit. Anorg. Chem. 25, pp. 1, 1900), and by Guntz and Feree (Compt. rend. 131, pp. 182, 1900), it was shown that more concentrated amalgams separated from solution at higher temperatures. That temperature was a factor in the concentration was therefore recognized by earlier workers in this field; but the prevailing idea of the effect of temprature in electrolytic preparation was that at certain temperatures the amalgam became stiff or solid, and was therefore impenetrable to the inflow of more potassium ions. For example Bain and Withrow (Jour. Phys. Chem. 25, pp. 542, 1921) state that "a cool electrolyte would produce a solid block of amalgam which could not of course be enriched to any extent on account of the impenetrability to newly discharged potassium ions." Shepherd (Jour. Phys. Chem. 7, pp. 29, 1903) had the same idea, for in referring to the work of Kurnakow (Zeit. Anorg. Chem. 23, pp. 439, 1900) he says "Since a 1.5% amalgam is solid at 25°c. and a 2% amalgam stiff at 100°c., we should hardly expect to

prepare a richer amalgam even though the 10% amalgam only melts at 100°c."

Shepherd seems to mean by this that if a 2% amalgam is stiff at 100°c. while a 10% amalgam is theoretically possible at 100°, still it would be impossible to pass from a 2% to a 10% amalgam electrolytically because of the impenetrability of the stiff amalgam to sodium ions. Shepherd was probably misled, however, by a misinterpretation of Kurnakow's diagram. The 10% referred to by Kurnakow was atomic per cent, meaning $NaHg_9$, or one atom of sodium in ten. Shepherd's 2% and Kurnakow's 10% are probably the same point on the diagram. No doubt this error in reading the diagram discouraged Shepherd from attempting further work for the realization of higher concentrations, and the publication of his work has also doubtless misled other investigators who otherwise might have solved the problem of stronger amalgams. This is all the more probable in view of the fact that the temperature factor is effectively obscured by other difficulties of manipulation which prevent its being evident.

Kurnakow's curve is a temperature-concentration diagram. Two facts in regard to the diagram (see Figure III) should be especially noted: First, the steepness of the curve on the right, showing that only a slight increase in the amount of potassium in the mercury is accompanied by a very considerable rise in the melting point of the amalgam. Second, after equal atomic amounts of potassium and mercury are reached at 270°c. further increase in potassium is accompanied by a fall in the temperature of the melting point.

Potassium and mercury constitute a two component system of the second class, and Kurnakow's curve suggests in part the familiar temperature-concentration diagram of ferric chloride and water. (Roozeboom, Zeit. Phys. Chem. 10, pp. 477, 1892). The phase rule offers a ready explanation of the failure of previous investigators to obtain a more concentrated amalgam by electrolytic methods.

For instance, working with ordinary laboratory apparatus and electrolyzing salt solutions of potassium at 4-6 amperes and 8-12 volts, as was usually the case for reasons of convenience, a temperature of 60°-80°c. in the electrolyte is attained. According to the diagram, at this temperature the compound KHg_9 is formed, which should dissolve in the mercury. If the experiment is continued long enough at a temperature of 70°c. all the mercury should be converted over to KHg_9, according to the phase rule diagram, in which

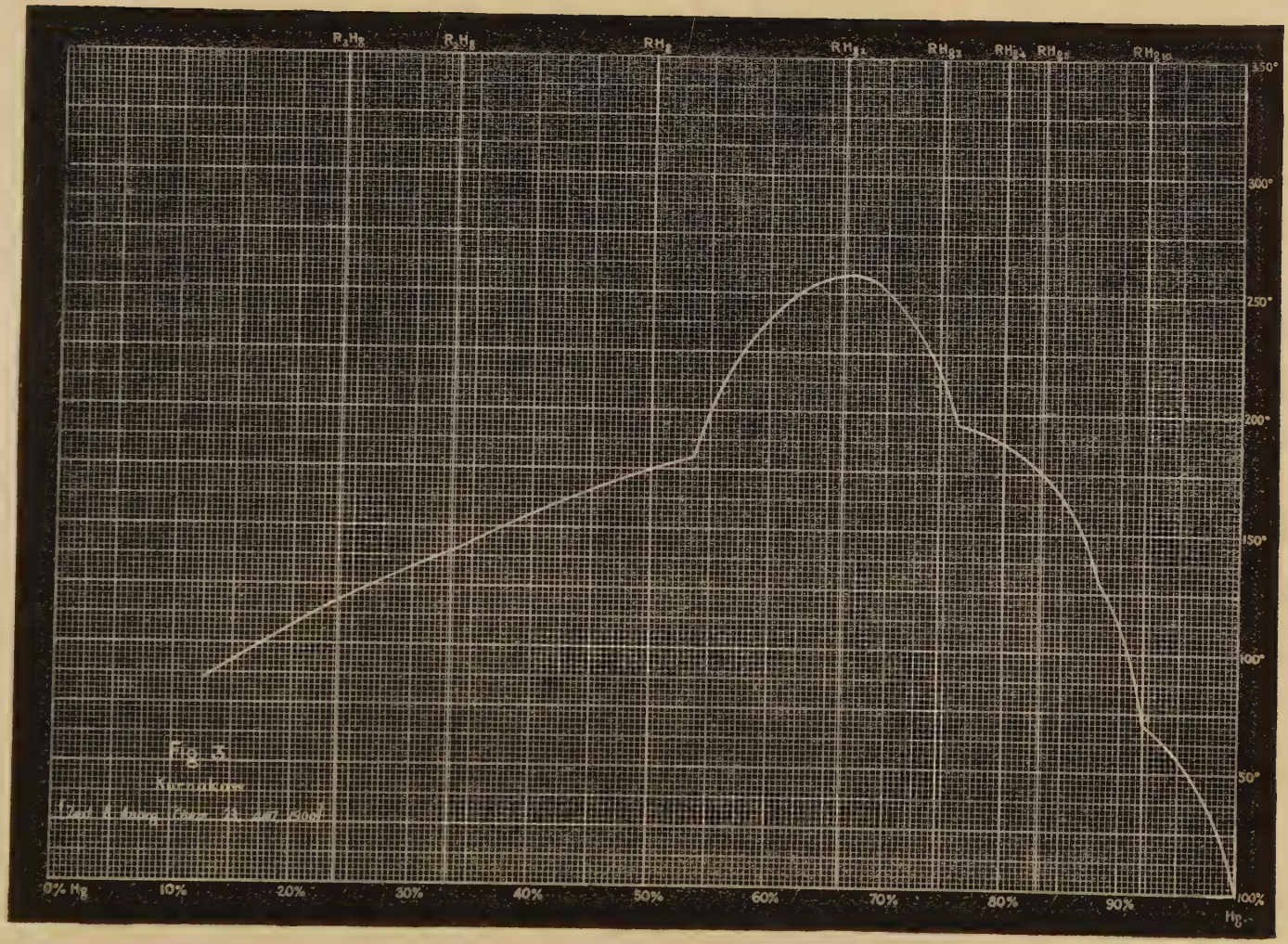
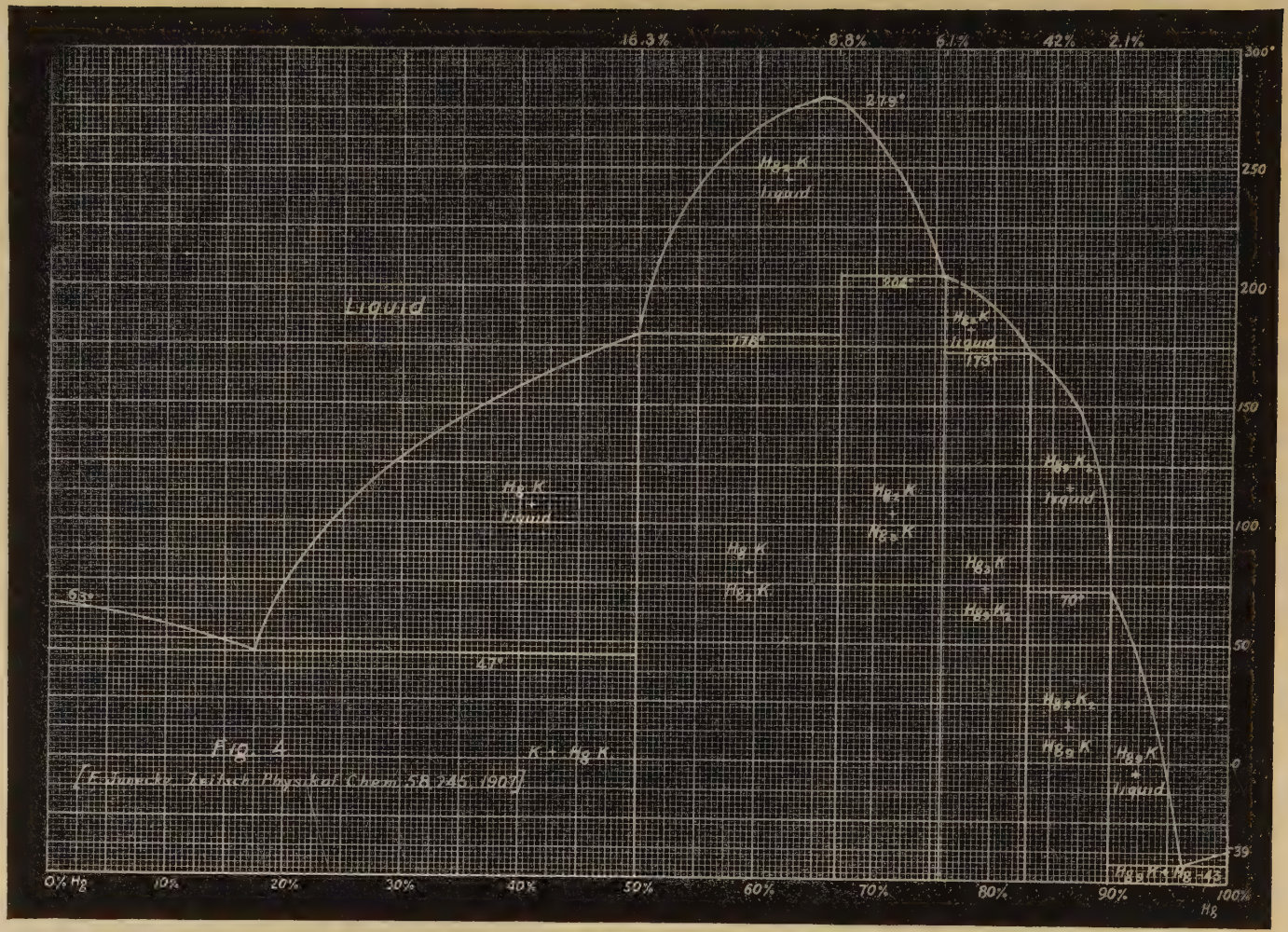

R_2Hg
R_4Hg_5
RHg
RHg_{12}
RHg_{20}
RHg_{24}
RHg_{28}
RHg_{40}
350°
300°
250°
200°
150°
100°
50°
0% Hg
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Hg

Fig. 5.


16.3%
8.8%
6.1%
42%
2.1%
300°
250
200
150
100
50
0
-39°
219°
Liquid
Hg_2K
Liquid
280°
Hg_2K
Liquid
178°
Hg_2K_3
Liquid
Hg_2K
Hg_3K
Hg_2K
Hg_3K
Hg_3K_4
70°
Hg_3K
Hg_5K_2
Hg_5K
Hg_9K
Liquid
95°
47°
Hg_5K_2 43°
Hg
0% Hg
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Hg
Fig. 4
K = Hg K
[E. Stanecki, Zeitsch. Physikal. Chem. 58, 245, (1907)]

case the mercury hardens in the cup and will analyze approximately 2.3% potassium. This, it is to be remembered, is the maximum concentration recorded in the literature. Usually this value is not reached because of auxiliary limiting factors such as injury to the cell, decomposition of the amalgam by the electrolyte, etc. If the temperature is raised, the diagram shows that the solid amalgam should melt, but the solubility of potassium in the melt is only slightly increased thereby because of the steepness of the liquidus curve. Further electrolysis under these conditions quickly saturates the liquid, and the excess potassium should deposit on the outer surface of the solid amalgam produced. Here KOH can be expected to form from the reaction of the metal with the water of the electrolyte. In fact this was observed to happen in several experiments under similar conditions.

The temperature-concentration diagram rises so steeply that no considerable increase in the metal content can be expected till the next break in the curve occurs. Here, at 173 degrees the compound K_2Hg_9 is the stable phase formed. If electrolysis is carried out at this temperature it should be possible to achieve a concentration of about 4.15% potassium, whereupon the behavior of the system should be the same as for KHg_9. It follows that for an increase in potassium content of only two per cent an increase in temperature of 103 degrees is required, and it can readily be understood why previous workers noted little temperature effect. At 204°c. K_3Hg_9 forms, making possible a concentration of about 6.1% potassium. The maximum temperature on the curve is 270°c. which corresponds to the compound KHg_2 with approximately 8.8% potassium. From this point the curve descends to 178°c. represented by KHg with 16.3% of alkali metal. It is to be noted that the concentration of potassium in these compounds rises in **geometrical progression with each 100° rise in temperature.**

Evidently, if the above reasoning is correct, it should be possible to obtain highly concentrated amalgams, provided a high enough temperature is maintained during electrolysis to prevent the separation of solid amalgam. While earlier workers mentioned the hardening of amalgams, they were not aware of the enormous rise in temperature necessary to maintain the amalgam liquid as the potassium content increased, as developed by the phase rule diagram.

Certain of the experiments on the effect of cell clogging and the effect of changes in the electrolyte on concentration had pointed

to the value of working at higher temperatures. For instance, two of the amalgams hardened in the cup at 100°c. and 120°c. respectively. The first analyzed 2.64% potassium. The second met with an accident and was not analyzed. Twelve other amalgams made by the Shepherd method hardened from room temperature to 90°c. and were found to have a smaller potassium content than the one hardening at 100°c.

D. Experimental Investigation of Electrolysis at High Temperatures

1. **High Temperature Electrolysis with the Shepherd Method.** With the experimental work pointing to temperature as the solution of the problem, an effort was accordingly made to follow up these results by making runs at much higher temperatures than had heretofore been used. Since a KCl solution saturated at room temperature boils off above 120°c. it was necessary to find another electrolyte.

Potassium acid sulfate dissolved in sulfuric acid gave a high boiling electrolyte, but it formed a glaze on the cells which rendered them non-conducting. Concentrated KOH solutions likewise gave a sufficiently high temperature, but were found to dissolve the cells in a half hour. The life of the cells could be prolonged by dissolving SiO_2 in the KOH solution, but such treatment caused excessive foaming of the electrolyte which could not be overcome sufficiently to make a satisfactory run. Finally, efforts to raise the temperature with the porous cup method were abandoned, and attention turned to the Smith-Bennett method.

2. **High Temperature Electrolysis with the Smith-Bennett Method.** From 50 to 100cc. of electrolyte was used in this series of experiments, with about 165 grams of mercury. Four to five amperes of current at five to six volts was employed. Several types of cells were tried out, the only advantage of one over the other proving to lie in the greater efficiency of those with a small surface area. The cathode in these experiments gave a great deal of trouble. The glass tubing necessary to protect the platinum wire cathode connection from the electrolyte broke repeatedly, possibly due to sparking at the tip where the wire was sealed into the tubing. Furthermore the wire burned off frequently, due to short-circuiting in the cell. It was found necessary to keep the anode as close to the cathode mercury as possible, and as portions of the amalgam

solidified, the large volume of gas liberated lifted the solid amalgam till contact was made with the anode.

Some trouble was encountered in finding a suitable electrolyte. Potassium acid sulfate dissolved in sulfuric acid was unsatisfactory, evidently because the acid decomposed the amalgam as fast as formed. Two runs were made with concentrated KOH solution. The solution was heated gradually up to 270°c. and the run continued for four hours. In this manner, two amalgams were obtained which analyzed 3.84% and 4.2% potassium. At 270°c. the amalgam rapidly attacked the electrolyte. In order to cut down the action of water in the electrolyte on the amalgam, 75 grams of molten KOH was used as an electrolyte, and 165 grams of mercury electrolyzed for three and a half hours at 270°c. In this manner an amalgam was obtained which analyzed 4.9% potassium and melted at 170 degrees. 6½ amperes of current at 4 volts was used. Calculation of the current efficiency shows that only 33-1/3% of the current was effective in the deposit of this amount of potassium. There was sufficient water present in the KOH to react violently with the amalgam in the bottom of the vessel. The source of the water in the molten KOH can be most readily explained by assuming the following reaction to have taken place:

$$2\ KOH \longrightarrow 2\ K + H_2O + O.$$

At any rate the boiling point of the electrolyte lowered as the run progressed, and it was difficult to maintain an even temperature.

As might be expected, the material of the apparatus was rapidly attacked by the molten caustic, resulting in frequent breakage and ruining of the experiment. Even the platinum anode was attacked by the caustic. Soon after starting a run, the electrolyte became black, mostly due to the formation of mercurous oxide. Only by the most careful manipulation, and the closest attention to the experiment, was it possible to complete a run.

The results of a number of these runs have been collected in Table No. II, in order that the relation of temperature to concentration made be brought out more fully. In view of these results, it seems fair to assume that previous investigators have failed to obtain more concentrated amalgams because they did not employ sufficiently high temperatures. Temperature may therefore be said to be one of the chief limiting factors in the concentration of electrolytically prepared amalgams.

TABLE II

Effect of Temperature on Concentration

Run No.	Sample No.	Method	Electrolyte	Volts	Amps.	Time Run	Temperature Electrolyte	Melting Point	% K
6	1	Shepherd	10% KOH sol	8-14	1-3	7½ hr.	—	75°c.	♯2.31
10	—	Shepherd	Sat. KCl	8-12	15	2 hr.	85°c.	70°c.	♯2.2
12	4	Shepherd	Sat. KCl	8-15	8-16	3 hr.	100-110°c.	95-100°c.	♯2.64
17	7	Shepherd	Sat. KCl	14-15	9-10	¾ hr.	120°c.	120°c.	♯3.2
18	8	Shepherd	Sat. KCl	8-10	4-6	2 hr.	90-100°c.	70°c.	♯2.2
21	10	Shepherd	Sat. KCl	10-14	4-6	7 hr.	100°c.	80°c.	♯2.31
30	—	Smith &	10% KOH sol	5-6	7-10	1 hr.	120°c.	45°c.	♯1.6
32	16	Bennett	10% KOH sol	6-12	5-10	3 hr.	120°c.	70°c.	2.2
34	—	Bennett	Conc. KOH sol	10	5½	2½ hr.	90-95°c.	68-70°c.	♯2.1
42	22	Shepherd	Conc. KOH sol	10	2	4 hr.	130°c.	110°c.	3.27
45	—	Smith &	Conc. KOH sol	8-10	5	2¼ hr.	190°c.	170°c.	3.84
46	23	Bennett	Conc. KOH sol	4	5	3½ hr.	190°c.	170°c.	3.84
47	24	Bennett	Molten KOH	3-4	5-6	4 hr.	190°c.	180°c.	4.2
50	25	Bennett	Molten KOH	4	6½	3½ hr.	190-230°c.	180-5°c.	4.9
101	51	Bennett	Molten KOH	4	2	3 hr.	95-100°c.	70°c.	2.1
103	52	Bennett	Molten KOH	6	6	9 hr.	100°c.	105-10°c.	3.09
104	53	Bennett	Molten KOH	6	6	3 hr.	100°c.	100-5°c.	2.98
105	54	Bennett	Molten KOH	5-7	5	14 hr.	100-200°c.	180-5°c.	4.95
106	—	Bennett	10% KOH sol	5-8	4	1 hr.	0	—	0.5

♯ From Temperature-Concentration diagram.

E. Equilibrium Between the Rate of Formation and the Rate of Decomposition as a Limiting Factor.

According to the temperature-concentration diagram, if electrolysis should be carried out at a point above 204°c. a concentration of 6.1% should be possible, and above 270°c. any value, 40%, 50%, 90%, or more might be obtained. Table II shows that the highest value actually attained was about 5%. After many trials, a few experiments were completed at this temperature maximum of 270 degrees, but the 5% concentration could not be exceeded. What factors were operating to limit the concentration in these experiments? There is reason to think that the probable answer to this question lies in the fact that with these more concentrated amalgams, the rate of the decomposition of the amalgam by the water of the electrolyte was sufficiently great to cause any increase in the potassium content to take place very slowly. A number of experiments can be cited in support of this conclusion.

1st. Amalgams with more than a small amount of potassium could not be made at all with sulfuric acid present in the electrolyte. According to Smith and Withrow, (Jour. Amer. Chem. Soc. 29, pp. 321) the most efficient electrolytes with respect to current consumption are KOH, KNO_3, KCl, and K_2SO_4, given in the order of their efficiency. This happens also to be the order for increasing hydrogen ion concentration in the electrolyte, since the second and third decompose on electrolysis to give off a gas. Evidently, then, the rate of decomposition of the amalgam by the electrolyte increases rapidly with increased hydrogen ion concentration in the electrolyte, and this rate might have a value sufficiently high to become a limiting factor.

2nd. Table II shows that the maximum concentration of potassium possible at the temperature of the experiment was not reached with KOH solutions. Furthermore, concentrated KOH solution proved a better electrolyte than a 10% solution of KOH; and at a temperature of 100 degrees, the more concentrated the solution the more efficient it was found to be. While it may be admitted that the increased potassium content of more concentrated solutions may have had an influence, it is reasonable to assume that the chief reason for the greater efficiency of concentrated solutions lay in their having less water available for the decomposition of the amalgam.

3rd. Whenever, during a run with molten KOH as an electrolyte, the current was shut off, the highly concentrated amalgam could be seen to be reacting violently with the molten KOH. This reaction was more rapid at higher temperatures when the amalgam was more concentrated.

It would appear possible to make measurements and plot curves showing the relation of temperature to rate of decomposition, and the relation of potassium content to rate of decomposition. With these values at hand, and knowing the current density employed, a fairly accurate idea should be had as to whether the rate of formation was being counteracted by the rate of decomposition. How-

ever, harder amalgams decomposed sometimes more rapidly, sometimes less rapidly than softer amalgams. Two samples of the same amalgam under what seemed to be identical conditions, frequently gave quite different amounts of hydrogen of decomposition over the same time interval, as though some form of catalysis or polarization were active. Finally, while in general, increase in temperature caused increase in the rate of hydrogen evolution, otherwise concordant results were never obtained.

As to the theory just mentioned that at temperatures above 200 degrees, the rate of decomposition equalled the rate of formation, attention should be called to one discordant fact. It is a well recognized principle of Physical Chemistry that in a general way, the velocity of a reaction doubles with a rise in temperature of ten degrees centigrade. In any case, it would be expected that a rise of thirty or forty degrees would make a considerable difference in the rate of decomposition of the amalgam at temperatures above 200 degrees. Therefore, if the temperature were maintained at 240°, decomposition should be more rapid than at 200°, and a softer amalgam result. This did not prove to be the case, and it seemed to make no difference whether the temperature was kept at 200° or 270°. Two explanations of the failure to decompose more rapidly at 270° than at 200° are possible. First, KOH is a very viscous solution at these temperatures, and water evaporates off slowly. The concentration of water present may therefore have remained practically constant at these widely different temperatures, thus controlling the rate of the reaction. In the second place, it might also be suggested that under these conditions, the increased velocity of the potassium ions due to increased temperature was sufficient to take care of any increase in the rate of decomposition.

IV. NOTES ON THE ELECTROLYTIC PREPARATION OF SODIUM BARIUM AND CALCIUM AMLAGAMS

In the course of the investigation of the factors limiting the concentration of potassium amalgams, opportunities arose for running some experiments of a miscellaneous character on other amalgams. With the problem of potassium amalgam giving promise of solution, advantage was taken of these opportunities to see whether the evidence which was accumulating for potassium would shed additional light on the old problems involved in the preparation of other alkali and alkaline earth amalgams by electrolytic methods. The resulting investigations are accordingly appended.

A. **Sodium Amalgam.** Between 70 and 139 degrees the temperature-concentration diagram for sodium as given by Kurnakow (Zeit. Anorg. Chem. 23, pp. 447, 1900) coincides closely with that for potassium. But for potassium, when starting with mercury itself, the first solid phase produced melts at 70 degrees and corresponds to the formula KHg_4, making possible at this temperature a maximum concentration of 2.3% potassium. The first solid phase produced for sodium, on the other hand melts at 151 degrees with the formula $NaHg_8$, corresponding to a concentration of 4.4% sodium. As commonly expressed in the literature, sodium is a softer

amalgam. Therefore, at 70 degrees, electrolysis should yield twice as concentrated an amalgam with sodium as is possible for potassium. This was verified experimentally. Using the Shepherd method, with 5 amperes of current at 7 volts, and with a saturated solution of sodium chloride at 75°c. an amalgam was obtained in an hour and a half which analyzed 4.1% sodium. The highest previously recorded concentration was 3.2%. The 4.1% sodium amalgam was solid at 60°c. A still harder amalgam was made in the same way, which hardened at 110°c. but was not analyzed, due to its being lost by the breaking of the container in which it was stored.

Barium Amalgam. The Shepherd method was used, with $BaCl_2$ as an electrolyte. Efforts to make this amalgam were not very satisfactory, owing to the fact that the alundum cups were not available at the time of the experiment. Three products were formed inside the cup: Barium hydroxide mixed with fine particles of mercury, large cubical crystals of barium amalgam, and a graphite like mass of mercurous oxide which adhered to the walls of the cup and clogged the pores. In six hours time only 20% of the mercury was converted to crystalline amalgam.

Calcium Amalgam. The literature does not record a single successful effort to produce calcium amalgam by electrolytic methods. The concensus of opinion is that the calcium amalgam is so reactive as to decompose as fast as it is formed. It was suggested by Bain and Withrow (Jour. Phys. Chem. 25, pp. 544) that electrolysis at low temperatures might slow up the reaction of the amalgam with the electrolyte to such an extent as to make possible its preparation. There is some reason to doubt these conclusions. In the first place, calcium is a less active metal than either sodium or posassium, and it is difficult to see why calcium should react more rapidly with the electrolyte. Nevertheless it can not be denied that the evidence in the literature shows its preparation by electrolytic methods to be extremely difficult or impossible.

Experiments were made with calcium amalgam made by direct union. These showed that calcium amalgam reacts less rapidly in both neutral and acid medium than amalgams of the alkali metals. As to the effect of low temperature, electrolysis carried out over a temperature range of -10 to 170 degrees with calcium chloride solutions showed little temperature effect.

A long series of experiments was made in the effort to produce calcium amalgam electrolytically. These were directed along two lines:—First, an attempt to carry out electrolysis at high temperatures. Second, an attempt to eliminate the effect of water on the amalgam.

1. **Electrolysis at High Temperatures.** No temperature-concentration curve has been recorded for calcium amalgam. Fortunately, however, the work of L. Cambi and G. Speroni (Atti R. Accad. Lincei 1914 (5) 23, II, pp. 599-611) may be used to give us some idea as to the probable nature of the curve. Though they plotted no curve, a partial one has been constructed from their

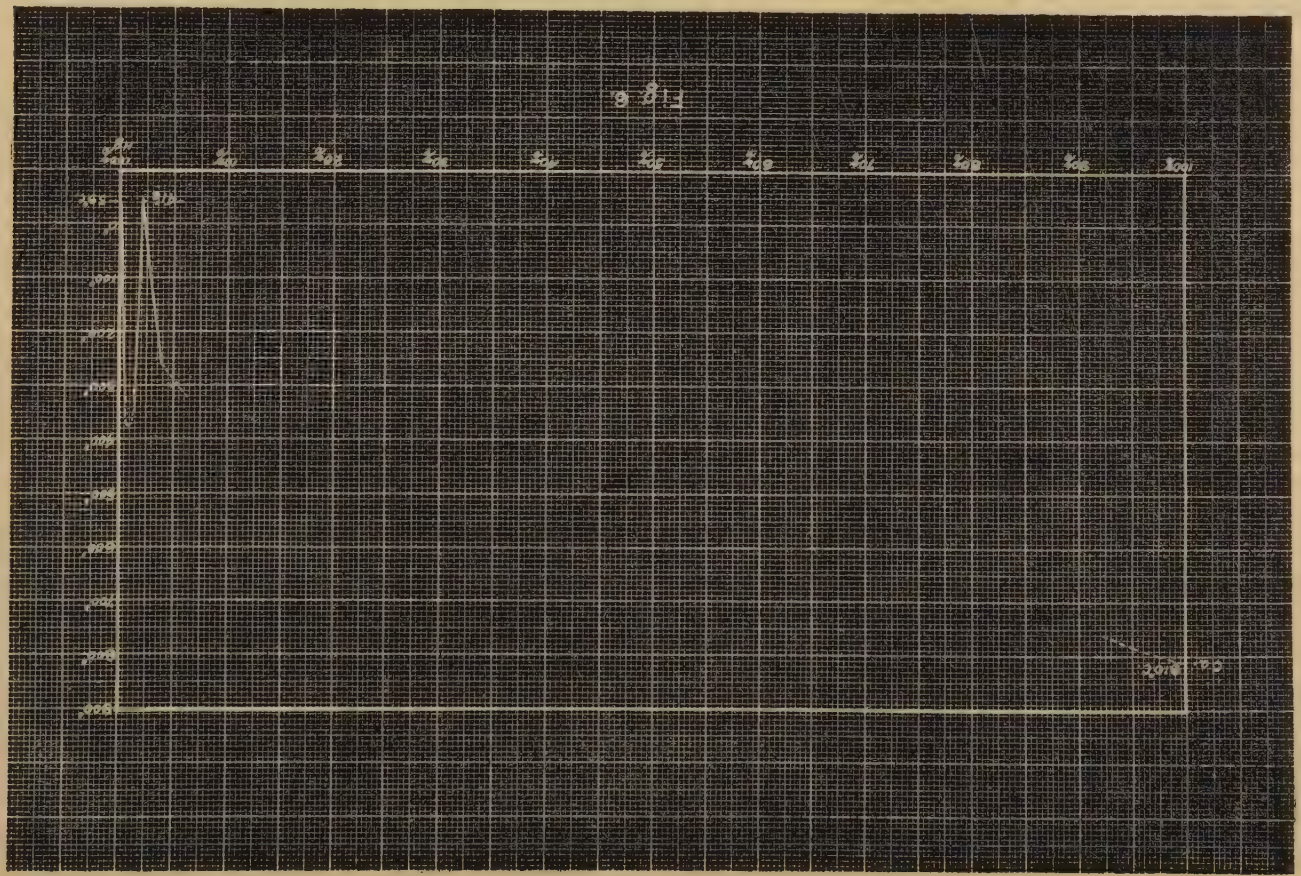
work. This is represented in figures 5 and 6. These authors propose the compounds $CaHg_4$ melting at 266 degrees with 4.8% calcium; and $CaHg_9$ melting at -41 degrees with 2.1% calcium. From this point on, the melting temperature rises rapidly with increased mercury or decreased calcium content until, when the calcium content is less than 1.5%, the amalgam only partially melts, and boils off at 377°c. In other words, incongruous melting takes place here as brought out by the accompanying diagrams.

Assuming the above facts to be true, and there is every reason to believe that they are approximately correct, the difficulty in preparing calcium amalgams electrolytically finds a ready explanation. For, reasoning from the phase rule, if we electrolyze at any temperature from the freezing point of mercury to 377 degrees, a solid begins to separate out when only a minute concentration of calcium has been reached, and it will continue to separate out till all the mercury has been changed to this form. It is probable that this compound is present to some extent at least in the gray, graphite like mass which is a frequent product of the attempt to make calcium amalgam.

Although Moissan says (Compt. rend. 127, pp. 584, 1898) that calcium and mercury combine at ordinary temperatures, this is not in agreement with the work of the Italian chemists just cited. In the progress of this investigation of the limiting factors a number of samples of calcium amalgam were made by direct union. It was found that a temperature of 318 degrees centigrade was necessary to effect combination. Fine particles of calcium kept submerged under the surface of the mercury at 310 degrees for several hours yielded only a trace of calcium in the mercury. However, as good a sample of metallic calcium as desired was not available for this work.

A careful review of the literature disclosed no compound or mixed salt of calcium with a fusion point between 300 and 400 degrees. Calcium chloride, melting in its own water of crystallization, produced the highest temperature—170°c. Above this temperature it lost the last molecule of water of crystallization and solidified. Salts of calcium either decompose at the temperature required, or fuse far above the boiling point of mercury. Calcium sulfate in sulfuric acid, and calcium phosphate in phosphoric acid provided electrolytes in which the temperature could be maintained above 300 degrees but electrolysis in these solutions failed to yield an amalgam, due to the presence of the acid.

2. **Efforts to Eliminate the Action of Water on the Amalgam.** The action of water on the amalgam during electrolysis might be reduced to a minimum provided electrolysis were to be carried out in non-aqueous solutions, or a non-aqueous solution were interposed as a layer between the mercury and the electrolyte. Since, in general, organic liquids are non-ionizing solvents, neither of these methods promised success.



However, the following electrolytes were tried out:

Calcium Salt		Organic Solvent
		Quinoline
Calcium acetate		Pyridine
Calcium chloride	in	Resorcine
Calcium nitrate		Pyrogallic acid
		Ortho cresol
Calcium oxide		Phenol salicilate

Pyrogallis acid with calcium acetate furnished the only satisfactory electrolyte, but it charred badly with more than weak currents. No amalgam was produced with an indicated concentration of more than .01%.

Experiments were made with the following liquids used as a protecting layer over mercury:

Quinoline	Resorcine
Pyrogallic acid	Ortho cresol
O. Brombenzene	Pyrogallic acid with $CaAc_2$
Phenol salicilate	Carbon tetrachloride

The method was not successful. If the layer was heavy enough to protect the mercury, the cell was rendered non-conducting. With thin layers, the evolved gases pushed aside the protecting layer and permitted contact between the water and the mercury. It was thought worth while to try out the Shepherd method with a protecting layer over the mercury.

When the cell walls became saturated with the protecting liquid, the conductance dropped to a low value. It became evident also that the liquid would not protect the mercury along the cell walls where the calcium ions entered the mercury. However the best results of the series were obtained by this method. Using a 10% solution of calcium chloride as an electrolyte, 3-5 amperes of current at 10-15 volts, alundum cups, and brombenzene as a protective layer, an amalgam was obtained with an indicated yield of .2% calcium. That is, 50 grams of the amalgam required 25cc. of standard acid equivalent to .004 grams of calcium per cc. to decolorize the phenolphthalein used as an indicator. With the low concentrations of calcium obtained, it was not thought worth while to make more than the roughest estimate of metal present. But in order to be sure that the alkalinity was not due to sodium or potassium impurities in the electrolyte, the calcium was precipitated as the oxalate, according to the usual analytical procedure.

In view of these experiments, the only alternative which suggests itself is the electrolysis of aqueous solutions under pressure in order to secure a sufficiently high temperature, and in order to prevent the decomposition of the amalgam at high temperatures.

CONCLUSIONS

1. The principle limiting factor controlling the concentration of metal in electrolytically prepared amalgams is found to be the temperature at which electrolysis is carried out, because of the tendency of the solid phase to separate out at low temperatures, the exact location of which is to be found on the temperature-concentration diagram.

2. By using molten KOH as an electrolyte, it is possible to prepare an amalgam analyzing as high as 4.95% potassium. The most concentrated potassium amalgam previously recorded contained 2.31% of the metal. Sodium amalgams were prepared with 4.2% of the metal. The highest content previously recorded was 3.2% sodium. An amalgam of calcium was made with an indicated value of .2% calcium.

3. It was concluded that at higher temperatures, the rate of decomposition of the amalgam by the electrolyte equalled the rate of formation, and became a second limiting factor.

4. Changes in the electrolyte, and plugging of the pores of the cup in the Shepherd method were found to be only occasional or incidental limiting factors. With alundum cups pore clogging is reduced to a minimum.

5. Exhaustion of the electrolyte is shown not to be a limiting factor. With a current as high as three amperes in saturated salt solutions, rate of deposition of sodium and potassium is sufficiently great that the rate of decomposition does not become a limiting factor. If the hydrogen ion concentration is high, however, the rate of decomposition does become the limiting factor.

6. If the temperature-concentration diagram developed in this work from the data of Cambi and Speroni is accurate for calcium amalgams, it is evident that calcium amalgams made by the ordinary electrolytic cell will not yield a concentration greater than approximately .2% calcium.

AUTOBIOGRAPHY

I, Clare S. Martin, was born November 30, 1888, at Loogootee, Indiana. My elementary and High School education were received in the public schools of New Castle, Indiana, where I graduated from the High School in 1907. The same year, I entered The Ohio State University for the purpose of studying the Natural Sciences, receiving in 1911 the degree of Bachelor of Science from the College of Agriculture. Upon receiving this degree, I enrolled immediatly in the Graduate School, and spent the summer in special Botanical studies at the Lake Laboratory, Cedar Point, Ohio. Upon completing my work there I accepted a position as Science teacher in the High School at Moundsville, West Virginia. From 1912 to 1914 I taught science in the High School at Bryan, Ohio, resigning there to accept a similar position in Van Wert, Ohio, where I remained till the close of the Spring term in 1918. The following year, I taught Chemistry and Physics in the High School at Chillicothe, Ohio. Three of the intervening vacation periods were spent in continuing my graduate studies at The Ohio State University. Having in the meantime acquired some business experience and training in commercial analysis, I became interested in the industrial applications of chemistry, and upon being offered an assistantship in Chemistry, I entered The Ohio State University in 1919 to study Industrial Chemistry. I received my Master's Degree in 1920, and in 1923 completed the requirements for the degree of Doctor of Philosophy.